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A New Mechanism for Surface Diffusion: Motion of a Substrate-Adsorbate Complex

by

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A NEW MECHANISM FOR SURFACE DIFFUSION: MOTION OF A SUBSTRATE-ADSORBATE COMPLEX

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Abstract

We propose a new mechanism for diffusion of surface adsorbates in which motion of the substrate atoms to which the adsorbates are attached results in the motion of the substrate-adsorbate complex. We show an experimental example — the motion of self-assembled monolayers of $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ on gold which we have observed by recording time-lapse movies with scanning tunneling microscopy.

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Diffusion on surfaces is important in surface processes where adsorbates must reach special sites to undergo reaction, in film growth to allow epitaxial or other special growth modes, and in other surface phenomena such as etching, corrosion, and wetting [1–3]. Diffusion involving complex molecules, such as those in self-assembled monolayers (SAMs), has important implications because molecular films are being used in attempts to create complex, multifunctional surface architectures such as artificial receptor sites [4] and controlled-size transport channels [5]. The dynamics of formation and the stability of the structures will depend upon the diffusion of the adsorbates. In this regard, recent evidence indicates that mixed composition alkanethiolate SAMs on gold surfaces can undergo phase segregation into domains which show time dependent shapes and sizes [6]. Using time-lapse scanning tunneling microscopy (STM), we have discovered evidence for motion of adsorbate-surface complexes across the surface.

Substrates were prepared by evaporating (pressure = $1-6 \times 10^{-7}$ torr) gold onto hot (340°C) mica. Such surfaces are known to consist of large Au{111} terraces. SAMs of $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ were prepared by soaking the substrate in a solution of the thiol in ethanol ($1 \times 10^{-3}\text{M}$) for four days [7]. Companion samples on larger substrates were prepared in parallel and characterized by infrared reflection and X-ray photoelectron spectroscopies, and by ellipsometry in order to verify the monolayer quality. Experiments were conducted in air using a microwave-frequency-compatible, beetle-style STM with a low drift rate [8,9]. The samples were sufficiently conductive (through the 22\AA monolayer thickness) to allow use of the dc tunneling current to control the tip-sample separation. The passive drift rate of this microscope is $<1\text{\AA}/\text{min}$, which allows recording a series of time-lapse images of the same area for hours without drift correction. Images were recorded in constant tunneling current mode. All images are shown unfiltered.

Fig. 1 shows such a series of 20 images of a $500\text{\AA} \times 500\text{\AA}$ area of the surface. After each image was recorded, the STM tip was repositioned at the center of the imaged area for 15 minutes before the next image was recorded. During both the delay and imaging periods the STM tip was biased at $\sim 2\text{V}$ with a tunneling current of 2 nA [10]. No special rearrangement of the surface exclusively at the center of the images was observed, and the rate of motion was independent of the delay period and

scan rate, showing that the STM tip did *not* drive the surface motion. It is important to note that the features (including steps) in the Au substrate are imaged *through* the thiolate monolayer [10], and thus the Au atoms and the thiolate layer move in a *concerted* manner.

The images in Fig. 1 are readily interpreted as a series of terraces separated by monatomic (single Au atom) height steps. The four to six steps in each frame appear as color changes. Fig. 2 schematically shows the positions of the step edges in selected frames of Fig. 1. Note the changes in the shapes of the step edges from frame to frame. The steps change shape and position between frames at a rate of approximately 10 atoms/site/hour along the step edges. This rate is substantially lower than that found for bare Au{111} in air by Mamin and coworkers and by Cooper and coworkers [12–14], and shows that the presence of the strongly bound thiolate monolayer [15,16] greatly increases the barrier to lateral motion. This is in sharp contrast to the observations of others that certain adsorbates appear to lower diffusion barriers. Trevor and Chidsey showed that strongly bound Cl adatoms accelerate the diffusion of surface Au atoms in aqueous solution [17,18]. Similarly, Cooper and coworkers found that (unidentified) adsorbates accelerated the motion of Au on the Au{111} surface in vacuum [13].

In order to correlate these various observations it is important to consider the adsorbate–substrate energetics. It has been shown that both chemisorbed S and Cl adatoms bind strongly to the Au surface atoms, thereby weakening the bonds between the attached Au atoms and their neighbors [17,18]. This would lead to more mobile surface Au atoms. On this basis, the thiolate S atoms should similarly allow fast surface diffusion of Au atoms; however, the opposite effect is observed. We therefore conclude that the underlying factor which controls the relative surface motion between thiolate and chloride is the adsorbate–adsorbate interaction [19]. This conclusion follows from the fact that attractive interactions between the alkyl chains in the alkanethiolates are large (compared to the Cl–Cl interactions). However, in order for such interactions to modulate the Au motion, it is necessary for motion to occur via an integral Au–thiolate complex. In this way chain–chain interactions can substantially reduce the motion of the “tethered” Au atoms.

Importantly, the above mechanism results in adsorbate diffusion which is fastest at sites with low coordination numbers for the Au surface atoms. In particular, the ability of a film with defects to approach an equilibrium structure thereby should be faster at a step edge than on a large Au{111} terrace. In accord with this we observe that on narrow terraces of the Au ($\leq 100\text{--}200\text{\AA}$ wide as in Fig. 1), few point defects in the film are found as compared to wider terraces. Point defects appear as $18\text{--}25\text{\AA}$ diameter, 1\AA deep depressions in STM images, which we ascribe to missing chain sites (molecular voids) with conformational relaxation of the surrounding matrix of alkyl chains [6,20]. It is critical to note that these molecular void defects on large terraces are never observed to move at room temperature. This argues against the ability of thiulates on terraces to move independently to step edges and supports defect annihilation by a fluctuating flow of step edges via motion of integral adsorbate–Au complexes. When the Au step edge reaches a molecular void defect site, the defect is swept off the terrace. In this way regions of missing thiolate can accumulate at step edges.

Supporting observations for the above molecular void defect removal mechanism are given in Fig. 1 which shows regions beneath the step risers that appear lower than the lower terrace heights. Fig. 3a shows the third frame of Fig. 1. One of these regions is visible as a blue (low) section in the image. Fig. 3b shows a cross section along the black line indicated in Fig. 3a. This cut shows two monatomic steps along with the associated depression below the step riser (indicated by arrows in Fig. 3b). Such depressions are not observed on the bare Au{111} surface. Going back to the frames shown in Fig. 1, these regions can be seen to change size and shape along the step edges with time. We assign the observed depressions at the step edges to two effects. First, the step edge breaks the translational order of the film at the boundary between the domains defined by the upper and lower terraces. This results in reduced density and conformational relaxation at this boundary. Second, these boundaries also function as the regions of the film in which missing chains are accommodated. The observed depressions have various depths and widths, because the density varies according to the number of molecular voids accommodated at any given region of the step edge. Also, the observed step motion is fastest at the site of the largest depressions, consistent with having fewer

neighbor alkanethiolate chains and less alkyl chain order (see below) thereby reducing the attractive interactions between chains.

Some data are available on the energetics of kink motion on step edges, and it is critical that the proposed thermally activated diffusion mechanism be consistent with these energetics. Kink-driven step edge motion is well known on fcc metal surfaces [18,21,22]. The activation energy for kink motion along the step edge of a large Ir cluster on clean Ir{111} has been determined by field ion microscopy measurements to be ~ 90 kJ/mole [22] as compared to the cohesive energy of Ir, 670 kJ/mole [23]. Scaling to the cohesive energy of Au, 368 kJ/mole, we can estimate this activation energy for bare gold to be 50 kJ/mole, identical to the measured upper limit of 50 kJ/mole reported by Trevor and Chidsey [17].

Bonding S or Cl atoms to the (001) faces of Ni and Cu reduces the bond strength of the bound metal atoms to their neighbors as evidenced by interlayer and intralayer relaxations and increased Debye-Waller factors in SEXAFS measurements [24]. Bonding of S or Cl to the Au{111} surface is expected to have similar consequences on the Au-Au bonding, leading to a small reduction of the cohesive energy of the bound Au atoms, which we estimate to be 10–15% [25]. We might further hypothesize that the transition state energy, and thus the activation barrier, have likewise been reduced by the same fraction. Using a simple Arrhenius activation energy dependence, and 50 kJ/mole for bare Au from above, the diffusion rate at room temperature would thereby increase by a factor of 7–20 upon chemisorption of Cl or S adatoms (the additional bonding of an alkyl chain to the S should reduce these effects somewhat).

Contrary to the accelerating effects of the S-Au bond on diffusion, the attraction between the alkyl chains should slow diffusion. The packing energy of a quasi-two-dimensional C_{16} alkanethiolate domain is ~ 74 kJ/mole [26]. This is approximately 1.3 times the attraction per methylene unit found for alkane liquids (from heats of fusion). To estimate this contribution to the activation energy due to the alkyl chain tether, we take the difference in the attraction between chains in the SAM (~ 74 kJ/mole) and in the alkane liquid (~ 57 kJ/mole), resulting in a value of ~ 17 kJ/mole [27]. The total activation energy for moving the gold-thiolate complex, we thus estimate to

be $\sim 59\text{--}62$ kJ/mole. We estimate that at room temperature this would reduce the rate of motion of the attached gold roughly by a factor of 1000 relative to bound Cl (or S), and by a factor of 100 relative to bare gold.

The stoichiometry of the diffusing complex remains unclear. Sellers *et al.* have calculated that the three-fold hollow site, sp^3 , thiolate species has almost the same energy as the atop, sp , species [28]. It may then be that the mobile thiolate–Au complex consists of the thiolate species attached to a single Au atom which moves along the surface as a step adatom. Further experiments are planned at reduced temperature to capture images of isolated hops in order to identify the diffusing adsorbate–substrate complex.

Finally, we point out that this adsorbate–substrate diffusion mechanism is consistent with other observations of alkanethiolate SAMs on Au. In particular, we have shown that mixed composition SAMs can phase segregate [6] and that motion of the adsorbed molecules is required to form the domains. The evidence presented here supports a mechanism of such motion involving an integral gold–thiolate complex [29]. This mechanism is also consistent with the proposal of Camillone *et al.* that the presence of mobile defects are responsible for thermal annealing of monolayer structures determined by He atom and X-ray diffraction [30].

In summary, we have shown that a molecular adsorbate can be transported across a surface via an integral substrate atom–adsorbate complex. It is likely that this mechanism is a general feature of surface diffusion of adsorbates which bind strongly to soft substrates such as the coinage metals. An additional example of this motion appears to be O adsorbed on Cu(110). On this surface, STM images have shown chains of O–Cu complexes moving cooperatively across the surface so as to coalesce into stripes of the O/Cu(110) 2×1 structure [31]. Unlike the motion along step edges described above, the chains of the O–Cu complex move on top of the Cu(110) substrate terraces.

We are currently quantifying the rates of motion due to this diffusion mechanism and determining how this mechanism influences the motion of defects in the SAMs. Further, we are working to compare the rates of motion for these C_{16} chains to those for shorter chains. By varying

the chain lengths, we anticipate being able to control the rates of motion by changing the attractive interactions between the alkyl chains [26].

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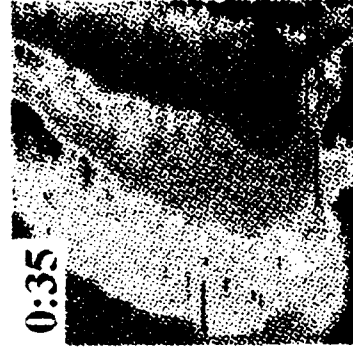
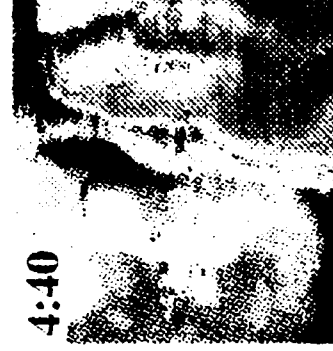
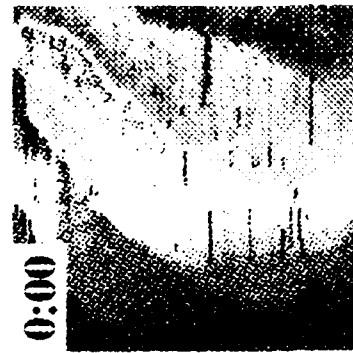
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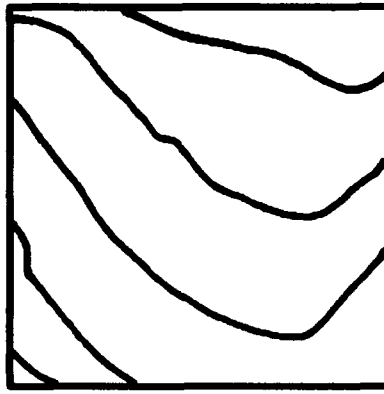
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FIGURE CAPTIONS

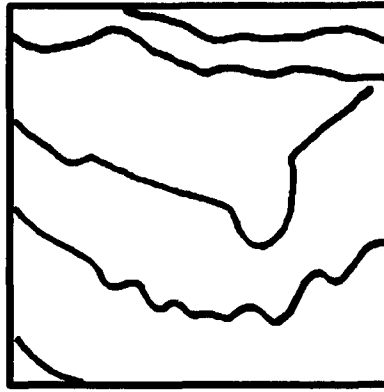
1. A series of 20 scanning tunneling microscope images showing a $500\text{\AA} \times 500\text{\AA}$ area of a SAM of $\text{CH}_3\text{O}_2\text{CC}_{15}\text{H}_{30}\text{SH}$ on Au. The images were recorded in air in constant current mode at a tunneling current of 2 nA and a tip bias of $\sim 2\text{V}$. Between each image the tip was positioned at the center of the area shown for 15 minutes. The start time is imprinted in each image as *hours:minutes*. A number of terraces each separated by a monatomic height step (2.5\AA) are shown. The color scale from top to bottom is: red, yellow, blue. The images are unfiltered.
2. Schematics of selected frames from Fig. 1 as indicated showing the motion of SAM-covered Au step edges over the sequence of images.
3. a. Frame 3 (0:35) from the series of $500\text{\AA} \times 500\text{\AA}$ images in Fig. 1, showing a line where the cross sectional view in b is taken. The color bar shows a 12\AA range.
b. A cross section along the line shown in a. Two monatomic height steps in the $\text{Au}\{111\}$ surface are shown. The "defect pools" are labeled with arrows.



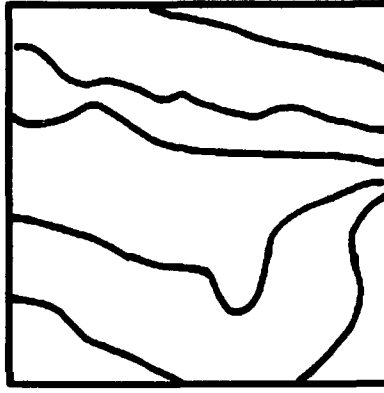
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